BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH *(Eichhornia Crassipes)*

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I declare that this dissertation entitled "*Biosorption of Chromium (VI) From Aqueous Solution By Dried Water Hyacinth (Eichhornia Crassipes)*" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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Date: 30 April 2009

Special Dedication to my family members,
my friends, my fellow colleague
and all faculty members

For all your care, support and believe in me.

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ABSTRACT

Metal ions in wastewater can cause serious toxicological problem which are dangerous to the environment and human being. Hexavalent chromium Cr (VI) is very toxic and mutagenic for most organisms. It is essential to remove this metal from wastewater. The purpose of this study is to investigate the performance of dried water hyacinth (*Eichhornia crassipes*) in biosorption of hexavalent chromium, Cr (VI). The effect of biosorbent dosage, initial concentreation, initial pH of the solution, and time contact were studied and the optimum conditions for biosorption process were indentified. Only the stems and leaves of the water hyacinth were use as the biosmass in this study. Biomass is mixed with the chromium solution at specific condition before the supernatant is taken. Supernatant were analyzed using atomic absorption spectrophotometer (AAS) in order to determine the concentration of chromium in the solution. Results show that biosorption of chromium (VI) highly depends on parameter studied. The amount of chromium adsorbed depends on the dosage. High loading of biomass will increase the removal of chromium. Low initial concentration also will make sorption yield higher. Biosorption of chromium (VI) is greatly depending on pH value because at pH more than, 2 the amounts of chromium remove is lower. When the time contact between biosorbent and solution increase, the removal of chromium also increase. The optimum condition for biosorption of chromium were at 0.7g biosorbent loading, initial concentration at 5mg/L, 1.8 pH value and 75 minutes of time contact.

ABSTRAK

Ion-ion logam di dalam air sisa buangan industri boleh menyebabkan masalah pencemaran toksik yang berbahaya kepada alam sekitar dan kehidupan manusia. Kromium Heksavalens, Cr (VI) adalah sangat toksik dan mutagenik kepada hampir semua organism. Oleh yang demikian kromium mesti diasingkan dari air sisa industri sebelum dibuang. Tujuan kajian ini adalah untuk menyiasat keupayaan keladi bunting (*Eichhornia crassipes*) yang telah dikeringkan dalam proses menjerap Kromium Heksavalens, Cr (VI). Parameter yang dikaji ialah kesan dos biomass, kepekatan ion kromium pada awal eksperimen, pH awal larutan, dan kesan masa terhadap proses menjerap kromium. Penjerap yang digunakan di dalam kajian ini adalah campuran batang dan daun keladi bunting. Penjerap dicampurkan dalam larutan kromium dalam keadaan tertentu bergantung kepada parameter yang dikaji seperti nilai pH dan dos biomas yg berbeza sebelum ditapis untuk mendapatkan sampel yang seterusnya dianalisa menggunakan AAS. Keputusan kajian ini menunjukan penjerapan Kromium Heksavalens bergantung kepada keempat-empat parameter yang dikaji. Keadaan yang optimum untuk penjerapan kromium adalah pada 0.7 g dos biomas, kepekatan larutan pada 5 mg/L, nilai pH 1.8 dan masa tindak balas pada 75 minit.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS/ABBREVIATIONS

AAS	-	Atomic Absorption Spectrophotometer
$K_2Cr_2O_7$	-	Potassium Dichromate
HCl	-	Hydrochloric acid
NaOH	-	Sodium Hydroxide
%	-	Percent
mg/L	-	milligram per liter
C_i	-	Initial Concentration
C_e	-	Concentration at equilibrium
Rpm	-	rotation per minutes

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The presence of extremely toxic elements can seriously affect plants and animals and have been involved in causing a large number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is unavoidable to search for different methods to reduce water pollution. The major sources of heavy metal contaminations are the industrial effluents. Due to their persistence in nature, it becomes essential to remove them from wastewaters. Various kind of heavy metal such as Lead, Zinc, Ferrum, Nickel, and also Chromium can be found in waste water.

Chromium containing solutions are used in a number of industries usually for chrome plating steels or for inhibiting corrosion in steel vessels. Because of the effect of the chromium to the environment, it is essential to treat wastewater contain Chromium before it can discharge to the drain system. Malaysian-Environmental Quality Act 1974 (Sewage and Industrial Effluents) 1979 stated that the concentration of Chromium (VI) in wastewater must below 0.05 mg/L for both standard A and standard B.

In this study, we use dried water hyacinth (*Eichhornia Crassipes)* as an adsorbent for biosorption of Chromium (VI) as an alternative method for conventional method for treating wastewater from industries that containing Chromium (VI). Biosorption make use of the ability of biological material to accumulate heavy metals from wastewater streams by either metabolically mediated or purely phsico-chemical pathway of uptake.

1.2 Problem statement

Wastewater from industry may contain dangerous and hazardous chemical. Wastewater from industries may cause pollution to the environment if this wastewater not treated seriously. The existence of heavy metal such as Chromium (VI) in the wastewater can caused toxic and mutagenic effect for most organisms. Before discharged to the drain system, this contaminated wastewater must be treated in order to make sure it is not harmful to the environment.

There are several way was developed in order to treat this wastewater and the common method is chemical precipitation using lime or caustic soda. Other method of treatment that available for wastewater treatment are such as ion exchange, electrolysis and reverse osmosis (RO) are high in operation cost and capital investment (V. K. Gupta *et al*., 1999). In this study, dried water hyacinth will be used as an adsorbent because this plant is a good biosorbent for removal of heavy metal like Chromium (VI) (Cycle Keith *et al*., 2006).

Treatment of wastewater using living water hyacinth need a large area such as water pond, and also can cause environmental problem. This plant can cause a problem like hindrance for water transport, microhabitat for a variety of disease factor such as mosquitoes, also reduction of biodiversity. In order to overcome this problem, it is possible to use dried water hyacinth in this study. Treatment using dried water hyacinth also is more convenient compare to using the living water hyacinth because it is easy for transportation of the biosorbent.

1.3 Objectives

Objectives of this study are:

1. To investigate the performance of dried water hyacinth as a biosorbent.
2. To study the biosorption of Chromium (VI) using dried water hyacinth.
3. To identify the optimum condition for biosorption of chromium (VI) using dried water hyacinth.

1.4 Scope of the study

To achieve the objectives stated above, the following scope had been identified:

1. Effect of pH.
2. Effect of dried water hyacinth dosage.
3. Effect of time.
4. Effect of initial concentration.

1.5 Rationale and Significance

In this study we want to remove the Chromium (VI) from aqueous solution by using dried water hyacinth. It is important to remove this heavy metal due to the environmental problem. The rationale we use dried water hyacinth in this study is because this plant is good for biosorption process based on previous finding of other researcher (Cycle Keith *et al*., 2006). The significance of these studies is to prove that dried water hyacinth can act as a biosorbent in biosorption process of chromium from aqueous solution.

From this study, the potential of dried water hyacinth as a biosorbent for removing Chromium (VI) from waste water can be utilized. Once the potential of water hyacinth in treating chromium containing solution proven, it can replace the conventional method of treating wastewater containing Chromium (VI). On the other hand, environmental problem caused by living water hyacinth can be solved because we used dried water hyacinth.

CHAPTER 2

LITERATURE REVIEW

This chapter will review the research and study that has already been done in order to gain information about this study. It provides background about wastewater, Chromium IV, biosorbent, biosorption and also biosorption mechanism.

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Wastewater from industry usually contains heavy metal such as Copper, Nickel and Chromium.

2.1.1 Wastewater Regulation

The electroplating industry has been reported as one of the major polluter to the environment. This industry generates pollutants such as heavy or trace metals including chromium (Parinda Suksabye, 1995). This heavy metal especially the Cr (VI) species has been known as toxic heavy-metal and being carcinogenic. Because of their high toxicity, the industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged to the environment. The industrial wastewaters must follow the limits as stated in the Environmental Quality (Sewage and Industrial Effluents) Regulations 1978. Table 2.1 show the limit of the parameter for standard A and standard B. Standard A is applied when wastewater is released at upper stream of the river and there is water intake to a Drinking Water Treatment Plant, while Standard B applied when wastewater released at the downstream of the river. This table below shows that for both standard A and B, wastewater must contain less than 0.05mg/L Chromium hexavalent.

Table 2.1: Environmental Quality Act 1974.

	Parameters	**Units**	**Standards**	
			A	**B**
1	Temperature	^{0}C	< 40.0	< 40.0
2	pH	pH	6.0 – 9.0	5.5 – 9.0
3	BOD_5 at 20 °C	mg/L	< 20.0	< 50.0
4	COD	mg/L	< 50	< 100
5	Suspended Solids	mg/L	< 50	< 100
6	Mercury	mg/L	< 0.005	< 0.05
7	Cadmium	mg/L	< 0.01	< 0.02
8	Chromium, hexavalent	mg/L	< 0.05	< 0.05
9	Arsenic	mg/L	< 0.05	< 0.10
10	Cyanide	mg/L	< 0.05	< 0.10
11	Lead	mg/L	< 0.10	< 0.50
12	Chromium, trivalent	mg/L	< 0.20	< 1.00
13	Copper	mg/L	< 0.20	< 1.00
14	Manganese	mg/L	< 0.20	< 1.00
15	Nickel	mg/L	< 0.20	< 1.00
16	Tin	mg/L	< 0.20	< 1.00
17	Zinc	mg/L	< 2.00	< 2.00
18	Boron	mg/L	< 1.00	< 4.00

Table 2.1 (Continued): Environmental Quality Act 1974

19	Iron	mg/L	< 1.00	< 5.00
20	Phenol	mg/L	< 0.001	< 1.000
21	Chlorine, Free	mg/L	< 1.00	< 2.00
22	Sulphide	mg/L	< 0.50	< 0.50
23	Oil & Grease	mg/L	Not Detectable	10.0

2.2 Chromium

The name of the element is derived from the Greek word "chrōma" (χρωμα) meaning color, because many of its compounds are intensely colored. It was discovered by Louis Nicolas Vauquelin in the mineral crocoite (*lead chromate*) in 1797.

Chromium is an element that can be found naturally in rocks, animals, plants, soil, and also in volcanic dust and gases. There are several forms of chromium that exist in our environment such as chromium (III), chromium (VI) and chromium (0).

Chromium (VI) or their compounds have been used extensively by various metal-finishing, mining and chemical industries. Chromium has characteristic that is high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium and nickel to form stainless steel. This has led to a sharp increase in the contamination of water. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water (Hamidi *et al*., 2007). Chromium is still widely used eventhough it has potential of toxicity.

2.2.1 Hexavalent Chromium

Hexavalent chromium refers to chemical compounds that contain the element chromium in the +6 oxidation state. Virtually all chromium ore is processed via conversion to sodium dichromate. Approximately 136,000,000 kg of hexavalent chromium was produced in 1985. Other hexavalent chromium compounds are chromium trioxide and various salts of chromate and dichromate. Hexavalent chromium is used for the production of stainless steel, textile dyes, wood preservation, leather tanning, and as anti-corrosion and conversion coatings as well as a variety of niche uses.

Hexavalent chromium is recognized as a human carcinogen via inhalation. Workers in many different occupations are exposed to hexavalent chromium. Exposure to chromium can occurs from ingesting the contaminated food or drinking water or breathing contaminated workplace air. High level of Chromium (VI) exposure can cause cancer and damage the nose. Ingesting large amount of Chromium (VI) can cause stomach upset and ulcers, convulsions, kidney and liver damage, and also possible of death.

2.2.2 Toxicity of Hexavalent Chromium

Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Trivalent chromium, which is the more common variety of chromium compounds, is not transported into cells.

Inside the cell, Cr (VI) is reduced first to metastable pentavalent chromium (Cr (V)), then to trivalent chromium (Cr (III)). Trivalent chromium binds to proteins and creates haptens that trigger immune response. Once developed, chrome sensitivity can be persistent. In such cases, contact with chromate-dyed textiles or wearing of chromate-tanned leather shoes can cause or exacerbate contact dermatitis.

Vitamin C and other reducing agents combine with chromate to give Cr (III) products inside the cell.

Hexavalent chromium compounds are genotoxic carcinogens. Chronic inhalation of hexavalent chromium compounds increases risk of lung cancer (lungs are especially vulnerable, followed by fine capillaries in kidneys and intestine). It appears that the mechanism of genotoxicity relies on pentavalent or trivalent chromium. According to some researchers, the damage is caused by hydroxyl radicals, produced during reoxidation of pentavalent chromium by hydrogen peroxide molecules present in the cell. Zinc chromate is the strongest carcinogen of the chromates used in industry. Soluble compounds, like chromic acid, are much weaker carcinogens. Figure 2.1 show an example of Chromium (VI) compound which is Chromium trioxide.

Figure 2.1: An example of a chromium (VI) compound: chromium trioxide

2.3 Biosorption

2.3.1 Introduction

Biosorption is processes that use the ability of biological material to accumulate heavy metal from wastewater stream by either metabolically mediated or purely physic-chemical pathways of uptake. Biosorption is a potential alternative to traditional treatment processes of metal ions removal. The phenomenon of biosorption has been showed in a wide range of non-living biomass like bark, lignin and peanut hulls as well as of living biomass like fungi, and bacteria also in living aquatic plant. One of these aquatic plants is water hyacinth (*Eichhornia crassipes).* Biosorption can also uses biomass raw materials which are either abundant such as seaweeds or wastes from other industrial operations like fermentation wastes. The major advantages of biosorption over other conventional treatment methods are lowcost, high efficiency of metal removal from dilute solutions, no additional nutrient requirements, regeneration of biosorbent, and possibility of metal recovery. (Kaustubha *et al*., 2005)

The biosorption process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass thus, the biosorbent becomes enriched with metal ions in the sorbate (Alluri *et al.*, 2007).

2.3.2 Biosorbent

Activated carbon has been standard adsorbent for treating wastewater for almost three decades. However, activated carbon remains an expensive material. There are various types of sources of biosorbent for biosorption process such as Seaweeds, microorganisms (bacteria, fungi, yeast, and molds), activated sludge, fermentation waste, and other specially propagated biomasses. Table 2.2 show that some of biomass that has been study for removal of Chromium (VI) from wastewater. Other biomass also has been studied for removing heavy metal from wastewater especially chromium (VI). This biomass are including, olive oil waste, rice husk and also seaweed. All of this biomass shows the potential of adsorption of chromium. However, some of these adsorbents do not contain high adsorption capacities. Biosorbents were characteristic as broad sources, low-cost, and rapid adsorption.

Table 2.1: Biosorbent use in Chromium (VI) removal

No	Heavy metal studied	Adsorbent	Parameter studied	References
1	Cu, Cr(VI), As	Living water Hyacinth	Concentration	Cycle Keith *et al.*(2006)
2	Cr(VI)	Dried Water Hyacinth	1.pH 2.Sorbent dose 3. Contact time 4. Initial Concentration	Kaustubha Mohanty *et al.*(2006)
3	Cr(VI)	Coir Pith	1.pH 2.Sorbent dose 3. Contact time 4. Temperature	Parinda Suksabye *et al.*(2006)
4	Cr(VI)	Green algae Spirogyra Speicies	1.Dose 2. Time contact 3. Initial concentration 4. pH	V.K. Gupta *et al.* (2001)
5	Cr(VI)	Red Algae (*Ceramium virgatum*)	1.pH 2.Sorbent dose 3. Contact time 4. Temperature	Ahmet Sari & Mustafa Tuzen (2008)
6	Ni(II), Zn(II), Cr(VI)	*Alternanthera philoxeriodes*	1.Particle size 1.pH 3. Contact time 4. Temperature	Xue-Song *et al.*(2006)
7	Cr(VI)	Coffe husk	1.pH 2.Sorbent dose 3. Contact time	Waleska E. Olieveira *et al.* (2007)